

Pedogenic stable W isotope fractionation in a Neoarchean weathering profile

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Empirical evidence from modern surface pools reveal stable W isotope fractionation beyond the range of ratios in igneous reservoirs [1] throughout the stages of chemical weathering and aqueous transport of soluble W species from land to sea [2-3]. Isotopically fractionated, authigenic W in marine shales suggests that at least some of the fractionation processes in operation also occurred at least as far back as the Paleoarchean [4]. However, there are insufficient data to constrain where fractionation began in ancient terrestrial environments and what processes drove fractionation. We present W-isotope data ($\delta^{186/184}\text{W}$) from the ca. 2.76 Ga Mt. Roe basalt-hosted paleosols (Fortescue Group, Western Australia) which indicate that surficial isotopic fractionation began as early as within terrestrial weathering profiles. Unlike other Precambrian paleosols for which there are robust elemental W data (low-blank, high-precision, uncompromised by tungsten-carbide milling) [e.g., 5], the Mt. Roe paleosol W data are decoupled from the post-depositionally enriched alkali elements, indicating that W was not overprinted by later metasomatic alteration. Upward depletion of W is accompanied by subtle but resolvable enrichment of lighter W isotopes and parallels the depletion of mobile major elements (Ca, Na, Mg, Fe) and P. Microanalytical data suggest W was preferentially leached from apatite and the basaltic groundmass relative to residual titanite (inferred to be a metamorphic product after igneous Fe-Ti-oxides), and leads us to hypothesize that W-isotopic fractionation was driven mainly by incongruent mineral weathering. The direction of fractionation in the paleosol is compatible with the heavier W isotope enrichment measured in black shales, including those deposited in direct association with the paleosol [4]. Collectively, these data point to a connected source-to-sink fractionation pathway for W in the low-O₂ Neoarchean surface environment.

[1] Kurzweil et al. (2019), *Geochim. Cosmochim. Acta* 251, 176-191.

[2] Kurzweil et al. (2021), *Proc. Natl. Acad. Sci.* 118, #e2023544118.

[3] Yang et al. (2022), *Geochim. Cosmochim. Acta* 322, 227-243.

[4] Roué et al. (2021), *Geochim. Cosmochim. Acta* 309, 366-